ITERATION-VARIATION PROCEDURES FOR QUANTUM MECHANICAL PERTURBATIONS*

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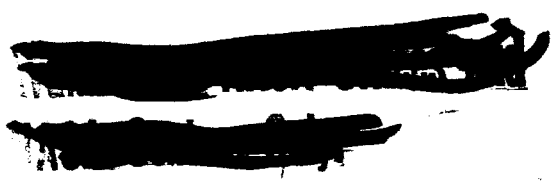
ABSTRACT 14325

The Dalgarno-Lewis procedure is used for obtaining explicit solutions to the perturbation equations. Three basic ideas are exploited: 1). By using the wave function through the first order as the zeroeth order wave function in a new perturbation calculation, we obtain an iteration procedure that converges with surprising rapidity. After n iterations, the energy is given accurately up to terms of the order of the 2^{n+1} power of a perturbation parameter. 2). By varying the proportions of the zeroeth and first order function in the wave function through the first order, we obtain somewhat better energies and still maintain the ability to iterate. And 3). For degenerate and almost-degenerate energy levels, the wave functions through the first order and the energies through the third order are obtained by solving a finite ordered secular equation. This procedure is much simpler and less apt to fail than the usual techniques.



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The Dalgarno-Lewis procedure[1] for determining explicit solutions to the perturbation equations has made it feasible to apply perturbation theory to a wide class of molecular problems where complete sets of solutions are not known for the unperturbed system. Perturbation treatments have the advantage over variational methods that they permit the system itself to select the proper type of terms which should be included in the trial wave function. From a knowledge of the trial wave function through the first order, the energy can be calculated accurately through the third order. For many chemical purposes this is sufficient accuracy.

The present paper contains three basic ideas:

1). By using the wave function through the first order as the zeroeth order trial function in a new perturbation calculation, we obtain an iteration procedure that converges with surprising rapidity. After n iterations, the energy is given accurately up to terms of the order of the 2^{n+1} power of a perturbation parameter.

2). By varying the proportions of the zeroeth and first order functions in the wave function through the first order, we obtain somewhat better energies and still maintain the ability to iterate.

3). For degenerate or almost-degenerate energy levels, the wave functions through the first order and the energies through the third order are obtained by solving a finite ordered secular equation. This procedure is much simpler and is less apt to fail than the usual techniques.

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The paper is divided into two parts. The first is concerned with the perturbation of non-degenerate energy levels. The second deals with degenerate or almost-degenerate problems.

PART I, PERTURBATION OF NON-DEGENERATE ENERGY LEVEL.

For quantum mechanical systems with a perturbation potential proportional to a parameter λ, a determination of the Rayleigh-Schrodinger perturbation wave function through the n-th order permits the determination of the energy accurately[2] through terms of the order of λ^{2n+1}. Much faster convergence without additional effort is obtained by a First Order Perturbation Iteration Method or FOPIM. This corresponds to using the Dalgarno-Lewis[1,3] procedure for determining the explicit first-order Rayleigh-Schrodinger perturbation wave function from a zeroeth-order function. The wave function through the first-order satisfies a Schrodinger equation and can be used as the zeroeth-order function in the calculation of an improved first-order function. The perturbation potential for this new calculation is proportional to λ^2. This process can be iterated and each time the new perturbation potential is proportional (in smallness) to the square of the previous perturbation potential. Thus, after n iterations, the energy is given accurately up to terms of the order of λ raised to the $(2)^{n+1}$ power. For example, after 5 iterations the energy is accurate up to terms of the order of λ^{64}.

Some additional improvement is obtained by a small modification which we might term FOP-VIM or First Order Perturbation-Variation Iteration Method. In FOP-VIM, following Dalgarno and Stewart[4], the perturbed wave function is taken to be the variationally best linear combination of the zeroeth order and Rayleigh-Schrodinger first order functions. This perturbed-variational function is then taken to be the zeroeth-order wave function for the calculation of an improved perturbed-variational function. Whereas FOP-VIM may have only a modest advantage over FOPIM for non-degenerate energy levels, we show in Part II that FOP-VIM is very useful for degenerate or almost degenerate energy levels.

A word of caution should be added in regard to the convergence of any perturbation scheme. Each problem must be examined separately. Some perturbation sequences diverge for physical reasons, as for example, the shift of the energy levels of a hydrogen atom placed in a uniform electric field. The energy levels become virtual energy levels as the result of the electric field and no stationary state solutions to the Schrodinger equation exist with the prescribed boundary conditions. Other perturbation sequences may diverge for purely mathematical reasons. In this case, a particular perturbation scheme may have a considerable advantage over another procedure. Usually, we might expect that the **FOPIM** and **FOP-VIM** should converge rapidly (either asymptotically or absolutely) if the second-order Rayleigh-Ritz perturbation energy is small compared to the first-order. Research on the convergence of perturbation methods is very much needed.

Rayleigh-Schrodinger Perturbation Theory for Non-Degenerate Energy Level.

Corresponding to an unperturbed Hamiltonian h, we know the q-th energy level $\epsilon_q(0)$ and its normalized eigenfunction $\psi_q(0)$. For present purposes, we assume that $\epsilon_q(0)$ is non-degenerate; in Part II, we consider the degenerate problems. The Schrodinger equation for the unperturbed system is then

$$h\,\psi_q(0) = \epsilon_q(0)\,\psi_q(0) \tag{1}$$

The Hamiltonian for the perturbed system is

$$H = h + \lambda V \tag{2}$$

The corresponding Schrodinger equation for the perturbed system is

$$H\,\Psi_q = E_q\,\Psi_q \tag{3}$$

We fix our attention on that perturbed state which, in the limit as λ approaches zero, has $\Psi_q = \psi_q(0)$ and $E_q = \epsilon_q(0)$. In order

to keep the notation from becoming too clumsy, the subscript q will be omitted except where it is necessary to avoid confusion between different energy states of the system.

In the Rayleigh-Schrodinger perturbation theory, Ψ and E are expanded in power series in the perturbation parameter,

$$\Psi = \sum_{n=0}^{\infty} \lambda^n \psi^{(n)}(0) , \qquad E = \sum_{n=0}^{\infty} \lambda^n \epsilon^{(n)}(0) \tag{4}$$

Clearly, $\epsilon^{(0)}(0) = \epsilon(0)$ and since the q-th energy level is non-degenerate, $\psi^{(0)}(0) = \Psi(0)$. Substituting these power series into Eq. (3) and equating the coefficients of each power of the perturbation parameter leads to the set of perturbation equations,

$$\left(h - \epsilon(0)\right)\psi^{(n)}(0) + \left(V - \epsilon^{(1)}(0)\right)\psi^{(n-1)}(0) = \sum_{j=2}^{n} \epsilon^{(j)}(0)\,\psi^{(n-j)}(0) \tag{5}$$

For the first-order perturbation equation with $n = 1$, the right-hand-side of Eq. (5) is zero.

Dalgarno and Lewis[2,3] found that in many cases the perturbation equations can be solved explicitly. Thus, defining a function F(0) such that

$$\psi^{(1)}(0) = F(0)\,\psi(0) , \tag{6}$$

the first order perturbation equation requires that

$$\left[F(0), H\right]\psi(0) = \left(V - \epsilon^{(1)}(0)\right)\psi(0) \tag{7}$$

or, if $\Psi(0)$ is real,

$$\sum_i \nabla_i \cdot \left(\psi^2(0)\,\nabla_i F(0)\right) = 2\psi(0)\left(V - \epsilon^{(1)}(0)\right)\psi(0) \tag{8}$$

Since Eqs. (7) and (8) do not specify F(0) to within an additive constant, we can require that $\psi^{(1)}(0)$ be orthogonal to $\Psi(0)$, or

$$\left(\Psi(0)\,,\ F(0)\,\Psi(0)\right) = 0 \tag{9}$$

The norm of $\Psi^{(1)}(0)$ is designated as $S(0)$,

$$\left(F(0)\,\Psi(0)\,,\ F(0)\,\Psi(0)\right) = S(0) \tag{10}$$

Using the first, second, and third order perturbation equations, it is easy to show that

$$\epsilon^{(1)}(0) = \left(\Psi(0),\ V\,\Psi(0)\right) \tag{11}$$

$$\epsilon^{(2)}(0) = \left(\Psi(0),\ V\,F(0)\,\Psi(0)\right) \tag{12}$$

$$\epsilon^{(3)}(0) = \left(F(0)\,\Psi(0), V F(0)\,\Psi(0)\right) - \epsilon^{(1)}(0)\,S(0) \tag{13}$$

The expectation value of the energy corresponding to the zeroeth order wave function is

$$E(0) = \left(\Psi(0),\ H\,\Psi(0)\right) = \epsilon^{(0)}(0) + \lambda\,\epsilon^{(1)}(0) \tag{14}$$

Let us define $\Psi(1)$ as the normalized wave function through the first order,

$$\Psi(1) = \left[1+\lambda^2 S(0)\right]^{-\frac{1}{2}}\left(1+\lambda\,F(0)\right)\Psi(0) \tag{15}$$

The expectation value of the energy through the first order is

$$E(1) = \left(\Psi(1), H\Psi(1)\right) = E(0) + \frac{\lambda^2\epsilon^{(2)}(0) + \lambda^3\,\epsilon^{(3)}(0)}{1+\lambda^2 S(0)} \tag{16}$$

Or, rearranging the terms,

$$E(1) = \epsilon(0) + \lambda\,\epsilon^{(1)}(0) + \lambda^2\epsilon^{(2)}(0) + \lambda^3\epsilon^{(3)}(0) - \frac{\lambda^4 S(0)\left[\epsilon^{(2)}(0) + \lambda\,\epsilon^{(3)}(0)\right]}{1 + \lambda^2 S(0)} \tag{17}$$

Comparing Eq. (17) with Eq. (4), it is apparent that E(1) is accurate up to terms of the order of λ^4. Everything up to this point is well-known and has been discussed in the literature[1]. The following treatment is novel.

FOPIM.

The wave function $\Psi(1)$ satisfies the Schrodinger equation

$$h(1)\,\Psi(1) = E(0)\,\Psi(1) \tag{18}$$

where

$$h(1) = h + \frac{\lambda V + \lambda^2 \epsilon^{(1)}(0)\,F(0)}{1 + \lambda F(0)} \tag{19}$$

The Hamiltonian for the perturbed system is then

$$H = h(1) + \lambda^2 V(1) \tag{20}$$

where

$$V(1) = \frac{F(0)\left[V - \epsilon^{(1)}(0)\right]}{1 + \lambda F(0)} \tag{21}$$

Now we consider the new perturbation problem in which $\Psi(1)$ serves as the zeroeth-order wave function and $\lambda^2 V(1)$ is the perturbation potential. Note that λ^2 plays the same role in the new problem as λ plays in the original problem. The new first-order perturbed wave function is

$$\psi^{(1)}(1) = F(1)\,\Psi(1) \tag{22}$$

where the function F(1) is determined by

$$\left[F(1), H\right]\Psi(1) = \left(V(1) - \epsilon^{(1)}(1)\right)\Psi(1) \tag{23}$$

or, if $\Psi(1)$ is real,

$$\sum_i \nabla_i \cdot \left(\Psi^2(1)\,\nabla_i F(1)\right) = 2\,\Psi(1)\left[V(1) - \epsilon^{(1)}(1)\right]\Psi(1) \tag{24}$$

The specification of the F(1) is completed by the requirement that

$$\left(\Psi(1),\ F(1)\,\Psi(1)\right) = 0 \tag{25}$$

The norm of $\Psi^{(1)}(1)$ is designated as S(1),

$$\left(F(1)\,\Psi(1),\ F(1)\,\Psi(1)\right) = S(1) \tag{26}$$

Using the first, second, and third order perturbation equations for the new perturbation problem,

$$\epsilon^{(1)}(1) = \left(\Psi(1), V(1)\Psi(1)\right) = \left[E(1) - E(0)\right]/\lambda^2 \tag{27}$$

$$\epsilon^{(2)}(1) = \left(\Psi(1), V(1)F(1)\,\Psi(1)\right) \tag{28}$$

$$\epsilon^{(3)}(1) = \left(F(1)\Psi(1), V(1)\,F(1)\,\Psi(1)\right) - \epsilon^{(1)}(1)\,S(1) \tag{29}$$

We can now define the second iterated normalized wave function

$$\Psi(2) = \left[1 + \lambda^4 S(1)\right]^{-\frac{1}{2}}\left(1 + \lambda^2 F(1)\right)\Psi(1) \tag{30}$$

The expectation value of the energy corresponding to $\Psi(2)$ is

$$E(2) = \left(\psi(2), H\,\psi(2)\right) = E(1) + \frac{\lambda^4 \epsilon^{(2)}(1) + \lambda^6 \epsilon^{(3)}(1)}{1 + \lambda^4 S(1)} \qquad (31)$$

Comparing Eq. (31) with the Rayleigh-Schrodinger perturbation expansion, Eq. (4), it is apparent that $E(2)$ is accurate up to terms of the order of λ^8.

The function $\psi(2)$ can now be used as the zeroeth order wave function in a new perturbation calculation. Indeed, after $(n+1)$ iterations we have the normalized wave function

$$\psi(n+1) = \left[1 + \lambda^{2a} S(n)\right]^{-\frac{1}{2}} \left(1 + \lambda^a F(n)\right) \psi(n) \qquad (32)$$

Here, because of printing difficulties, we use the notation $a = 2^n$. The $S(n)$ is the norm of $\psi^{(1)}(n)$,

$$\left(F(n)\,\psi(n), F(n)\,\psi(n)\right) = S(n) \qquad (33)$$

The function $F(n)$ satisfies the inhomogenous partial differential equation

$$\left[F(n), H\right]\psi(n) = \left[V(n) - \epsilon^{(1)}(n)\right]\psi(n) \qquad (34)$$

together with the requirement that

$$\left(\psi(n), F(n)\,\psi(n)\right) = 0 \qquad (35)$$

From the first, second, and third order perturbation equations for this perturbation problem it follows that

$$\epsilon^{(1)}(n) = \left(\psi(n),\ V(n)\,\psi(n)\right) = \left[E(n) - E(n-1)\right]/\lambda^{a} \tag{36}$$

$$\epsilon^{(2)}(n) = \left(\psi(n),\ V(n)\,F(n)\,\psi(n)\right) \tag{37}$$

$$\epsilon^{(3)}(n) = \left(F(n)\,\psi(n),\ V(n)\,F(n)\,\psi(n)\right) - \epsilon^{(1)}(n)\,S(n) \tag{38}$$

The expectation value of the energy corresponding to $\psi(n+1)$ is

$$E(n+1) = \left(\psi(n+1), H\,\psi(n+1)\right) = E(n) + \frac{\lambda^{2a}\epsilon^{(2)}(n) + \lambda^{3a}\epsilon^{(3)}(n)}{1 + \lambda^{2a}\,S(n)} \tag{39}$$

Comparison of Eq. (39) with the Rayleigh-Schrodinger expansion, Eq. (4), shows that $E(n+1)$ is accurate up to terms of the order of λ^{4a}.

The function $\psi(n+1)$ satisfies the Schrodinger equation

$$h(n+1)\ \psi(n+1) = E(n)\ \psi(n+1) \tag{40}$$

where

$$h(n+1) = h(n) + \frac{\lambda^{a} V(n) + \lambda^{2a}\epsilon^{(1)}(n)\,F(n)}{1 + \lambda^{a}\,F(n)} \tag{41}$$

The Hamiltonian for the perturbed system is then

$$H = h(n+1) + \lambda^{2a}\,V(n+1) \tag{42}$$

where

$$V(n+1) = \frac{F(n)\left[V(n) - \epsilon^{(1)}(n)\right]}{1 + \lambda^{a}\,F(n)} \tag{43}$$

The iteration scheme can then be continued through the next step.

FOP-VIM.

Following Dalgarno and Stewart[4], we can consider in place of $\Psi(1)$, the normalized function

$$\chi(1) = \left[1+\lambda^2\alpha^2(0)S(0)\right]^{-\frac{1}{2}}\left(1+\lambda\alpha(0)F(0)\right)\Psi(0) \qquad (44)$$

Here $\alpha(0)$ is a parameter which is chosen so as to make

$$\partial E'(1)/\partial\alpha(0) = 0 \qquad (45)$$

where

$$E'(1) = \left(\chi(1),\ H\chi(1)\right) \qquad (46)$$

For this optimum value of $\alpha(0)$, the energy $E'(1)$ is a solution to the secular equation

$$0 = \begin{vmatrix} E(0)-E'(1) & \lambda^2\epsilon^{(2)}(0) \\ \lambda^2\epsilon^{(2)}(0) & -\lambda^2\epsilon^{(2)}(0)+\lambda^3\epsilon^{(3)}(0)+\lambda^2 S(0)\left[E(0)-E'(1)\right] \end{vmatrix} \qquad (47)$$

There are two roots to this secular equation. However, only one of these roots corresponds to $E'(1)$ approaching $\epsilon(0)$ as λ approaches zero. Only this root can have physical significance for our problem,

$$E'(1) = E(0) + \left[\frac{\lambda^2\epsilon^{(2)}(0)-\lambda^3\epsilon^{(3)}(0)}{2\lambda^2 S(0)}\right]\left[\left\{1+\frac{4\lambda^6 S(0)\left[\epsilon^{(2)}(0)\right]^2}{\left[\lambda^2\epsilon^{(2)}(0)-\lambda^3\epsilon^{(3)}(0)\right]^2}\right\}^{-\frac{1}{2}}-1\right] \qquad (48)$$

Expanding $E'(1)$ and $E(1)$ in powers of λ, we find that

$$E'(1) - E(1) = \lambda^4\frac{\left[\epsilon^{(3)}(0)\right]^2}{\epsilon^{(2)}(0)} + \lambda^5\left[\frac{\left[\epsilon^{(3)}(0)\right]^3}{\left[\epsilon^{(2)}(0)\right]^2} - 2S(0)\epsilon^{(3)}(0)\right] \qquad (49)$$

$$+ \cdots$$

For the ground state, it is well known[1] that $\epsilon^{(2)}(0)$ is necessarily negative. Thus, for the ground state, $E'(1) - E(1)$ is negative. For other states, the sign of $E'(1) - E(1)$ is not known a-priori.

The optimum value of $\alpha(0)$ is

$$\alpha(0) = \frac{E'(1) - E(0)}{\lambda^2 \epsilon^{(2)}(0)} \tag{50}$$

Expanding in powers of λ,

$$\alpha(0) = 1 + \frac{\lambda \epsilon^{(3)}(0)}{\epsilon^{(2)}(0)} + \lambda^2 \left[\left(\frac{\epsilon^{(3)}(0)}{\epsilon^{(2)}(0)} \right)^2 - S(0) \right] + \cdots \tag{51}$$

The normalized function $\chi(1)$ satisfies the Schrodinger equation

$$h'(1)\ \chi(1) = E(0)\ \chi(1) \tag{52}$$

where

$$h'(1) = h + \frac{\lambda \alpha(0) V + \lambda (1-\alpha(0)) \epsilon^{(1)}(0) + \lambda^2 \alpha(0) \epsilon^{(1)}(0)\ F(0)}{1 + \lambda \alpha(0) F(0)} \tag{53}$$

The Hamiltonian for the perturbed system is then

$$H = h'(1) + \lambda^2 V'(1) \tag{54}$$

where

$$V'(1) = \frac{\left[\lambda^{-1} (1-\alpha(0)) + \alpha(0) F(0) \right] \left[V - \epsilon^{(1)}(0) \right]}{1 + \lambda \alpha(0) F(0)} \tag{55}$$

From Eq. (51) it follows that $\lambda^{-1}(1- \alpha(0))$ is zeroeth order in λ.

Clearly, in much the same manner as in FOPIM, the $\chi(1)$ can be used as the zeroeth order wave function to generate a new first order function

$$\chi(2) = \left[1 + \lambda^4 \alpha^2(1) S(1)\right]^{-\frac{1}{2}} \left(1 + \lambda^2 \alpha(1) F'(1)\right) \chi(1) \qquad (56)$$

Here $S'(1)$ is

$$S'(1) = \left(F'(1)\ \chi(1), F'(1)\ \chi(1)\right) \qquad (57)$$

The function $F'(1)$ satisfies the equation

$$\left[F'(1), H\right] \chi(1) = \left[V'(1) - \left(\chi(1), V'(1) \chi(1)\right]\right] \chi(1) \qquad (58)$$

together with the condition

$$\left(\chi(1), F'(1)\ \chi(1)\right) = 0 \qquad (59)$$

The parameter $\alpha(1)$ is adjusted so as to make $\partial E'(2) / \partial \alpha(1) = 0$ where

$$E'(2) = \left(\chi(2), H\ \chi(2)\right) \qquad (60)$$

This procedure may be iterated as often as desired or required.

The energy $E'(2)$ may be somewhat improved without much additional work. In place of $\chi(2)$, we can define the function

$$\omega(2) = \Psi(0) + \lambda \alpha' F(0) \Psi(0) + \lambda^2 \beta' F'(1) \chi(1) \qquad (61)$$

The constants α' and β' are adjusted so as to optimize the energy

$$E''(2) = \left(\omega(2), H\ \omega(2)\right) \Big/ \left(\omega(2), \omega(2)\right) \qquad (62)$$

The "best" value of the energy is that root of the three dimensional secular equation which reduces to $\epsilon(0)$ in the limit as λ approaches zero. This variation of the FOP-VIM can also be iterated.

Non-degenerate perturbation theory becomes inapplicable when two energy levels lie close together and interact strongly under the influence of the perturbation. In order to examine the explicit effect of some "o"-eth quantum state on the q-th state under consideration, let us form the trial wave function

$$\Phi(1) = \chi_q(1) + \lambda^2 C \psi_o(0) \tag{63}$$

The constant C can be adjusted so as to optimize the energy

$$\mathcal{E}_q = \left(\Phi(1), H\Phi(1)\right) \Big/ \left(\Phi(1), \Phi(1)\right) \tag{64}$$

In this, and the following paragraph, it is convenient to use the notation: $(X)_{ij} = (\psi_i(0), X\,\psi_j(0))$. In forming the matrix components for the two dimensional secular equation, the only special point to be noted is that

$$(F_q(0))_{oq} = (V)_{oq}/(\epsilon_q(0) - \epsilon_o(0)) \tag{65}$$

The constant C corresponding to the physically significant root of the secular equation is

$$C = \left(\epsilon_q(0) - \epsilon_o(0)\right)^{-2}\left[-\epsilon_q^{(1)}(0) - \left(\epsilon_q(0) - \epsilon_o(0)\right)\frac{\epsilon_q^{(3)}(0)}{\epsilon_q^{(2)}(0)} + \left(F_q(0)V\right)_{qo}\right] + \lambda[\cdots] + \cdots \tag{66}$$

Expanding the energy in powers of λ,

$$\mathcal{E}_q = E_q'(1) + \frac{\lambda^4\left[-\epsilon_q^{(1)}(0) - \left(\epsilon_q(0) - \epsilon_o(0)\right)\frac{\epsilon_q^{(3)}(0)}{\epsilon_q^{(2)}(0)} + \left(F_q(0)V\right)_{qo}\right]^2}{\left(\epsilon_q(0) - \epsilon_o(0)\right)^3} + \lambda^5[\cdots] + \cdots \tag{67}$$

Since $E'_q(1)$ is accurate through terms in λ^3, it is not surprising that the first corrections to $E'_q(1)$ should be proportional to λ^4. From Eq. (67) it follows that $\mathcal{E}_q > E'_q(1)$ if $\epsilon_q(0) > \epsilon_o(0)$ and $\mathcal{E}_q < E'_q(1)$ if $\epsilon_q(0) < \epsilon_o(0)$. For the ground state, the energy is lowered by the interaction with every other state.

If $|\mathcal{E}_q - E'_q(1)| > |E'_q(1) - E_q(0)|$, the expansion of $\mathcal{E}_q$ in powers of λ (as given by Eq. (67)) is no longer possible and the non-degenerate perturbation theory becomes inapplicable. In such cases, the almost-degenerate perturbation treatment given in Part II may be used.

For the ground state, the FOP-VIM energies $E'(n)$ or $E''(n)$ are greater than or equal to the exact energy for the perturbed system. As Sinanoglu has shown[5], similar variational principles can be established for the perturbed energy of the higher energy states provided that we know the set of unperturbed wave functions $\psi_k(0)$ for all of the states having energy less than $\epsilon_q(0)$. Thus, we define the wave function

$$\Omega_q(1) = \chi_q(1) + \sum_{K=1}^{q-1} \lambda^2 C_{Kq} \psi_K(0) \tag{68}$$

Here the summation extends over all of the quantum states whose unperturbed energy $\epsilon_k(0)$ is less than $\epsilon_q(0)$. The constants C_{kq} are varied so as to give the lowest energy

$$\mathcal{E}'_q(1) = \left(\Omega_q(1), H\Omega_q(1)\right) \Big/ \left(\Omega_q(1), \Omega_q(1)\right) \tag{69}$$

subject to the condition that as λ approaches zero, $\mathcal{E}'_q(1) = \epsilon_q(0)$. This entails the solution of a q-dimensional secular equation. The Löwdin partitioning technique[6] is particularly well-suited for the determination of the roots of this secular equation. Only one of these roots reduces to $\epsilon_q(0)$ when λ approaches zero. The other (q-1) roots are lower than $\mathcal{E}'_q(1)$. Thus, by MacDonald's theorem[7], we can be sure that the value of $\mathcal{E}'_q(1)$ is larger than the exact energy E_q.

Both the $\Phi_q(1)$ and the $\Omega_q(1)$ can be used as zeroeth order functions in a FOP-VIM sequence.

PART II, PERTURBATION OF DEGENERATE OR ALMOST DEGENERATE ENERGY LEVELS.

The usual Rayleigh-Schrodinger method can be exceedingly complex and difficult to apply to perturbation problems involving degenerate or almost-degenerate energy levels[1]. Greater accuracy and far greater simplicity can be obtained by the following procedure: DE-FOP-VIM, which is FOP-VIM generalized to apply to the degenerate and almost degenerate energy levels.

Corresponding to the Hamiltonian h for the unperturbed system, we are given the set of s linearly independent functions ϕ_k which form a complete set of eigenfunctions for each of the energy levels e_k under consideration. The e_k may all have a single value corresponding to a degenerate energy level or else they may have slightly different values corresponding to a closely packed group of almost degenerate energy levels. Since the states corresponding to different energy levels may interact under the influence of a perturbation, the larger the number of interacting states considered the greater is the accuracy. The Schrodinger equation for the unperturbed system is

$$h \phi_k = e_k \phi_k , \qquad k = 1,2,\cdots,s \tag{70}$$

The Hamiltonian for the perturbed system is

$$H = h + \lambda V \tag{71}$$

The corresponding Schrodinger equation for the perturbed system is

$$H \Psi_j = E_j \Psi_j \tag{72}$$

We fix our attention on those s states Ψ_j whose energies E_j approach the values of e_k in the limit as λ approaches zero. Let us define a set of functions G_k such that if ϕ_k were a zeroeth order wave function, then $G_k \phi_k$ would be a possible first order function. The Rayleigh-Schrodinger first order perturbation equation which determines G_k is

$$(h - e_k)G_k\phi_k + \left[V - (V)_{kk}\right]\phi_k = 0 \tag{73}$$

Here the notation $(P)_{ij}$ will be used to denote $(\phi_i, P\,\phi_j)$. Equivalent to Eq. (73), we can write

$$\left[G_k, H\right]\phi_k = \left[V - (V)_{kk}\right]\phi_k \tag{74}$$

Or, if ϕ_k is real,

$$\sum_i \nabla_i \cdot \left(\phi_k^2 \nabla_i G_k\right) = 2\,\phi_k\left[V - (V)_{kk}\right]\phi_k \tag{75}$$

The first approximation to Ψ_j can then be written in the form

$$\Psi_j(1) = \sum_{k=1}^{s}\left[\alpha_{j,k} + \lambda\,\beta_{j,k}\,G_k\right]\phi_k \tag{76}$$

The constants $\alpha_{j,k}$ and $\beta_{j,k}$ are chosen so as to normalize $\Psi_j(1)$ and optimize the energy

$$E_j(1) = \left(\Psi_j(1), H\,\Psi_j(1)\right) \tag{77}$$

The optimum values of $E_j(1)$ are given as s of the roots of the $2s$ dimensional secular equation

$$\begin{vmatrix} A & B \\ B^{\dagger} & C \end{vmatrix} = 0 \tag{78}$$

where $\mathbb{A}$, $\mathbb{B}$, and $\mathbb{C}$ are the s-dimensional sub-matrices with the elements

$$A_{ij} = (\phi_i, H\phi_j) - E(1)(\phi_i, \phi_j) \tag{79}$$

$$B_{ij} = (\phi_i, HG_j\phi_j) - E(1)(\phi_i, G_j\phi_j) \tag{80}$$

$$C_{ij} = (G_i\phi_i, HG_j\phi_j) - E(1)(G_i\phi_i, G_j\phi_j) \tag{81}$$

The Löwdin[6] partitioning technique is particularly well suited to the solution of such secular equations. The s roots which have physical significance reduce to the values of e_k in the limit as λ approaches zero. The other s roots have no significance for our perturbation problem. The values of the $E_j(1)$ obtained in this manner should be accurate through terms in λ^3 and somewhat more accurate than the Rayleigh-Schrodinger energies through the third order.

In the Rayleigh-Schrodinger treatment, all of the states under consideration have the same unperturbed energy. Almost-degenerate examples must be treated in a very artificial manner which effectively reduces them to true degeneracy[1]. The constants $\alpha_{j,k}$ are chosen by making a unitary transformation which diagonalizes the matrix $\mathbb{A}$. If, however, some of the first-order perturbation energies are degenerate, it is necessary to diagonalize sets of matrices which involve the second-order perturbation energy, etc. Thus the determination of even the $\alpha_{j,k}$ is complicated and the procedure depends a great deal upon the order of perturbation in which the degeneracy is removed. The determination of the $\beta_{j,k}$ is then easy. However, the functions $G_k\phi_k$ are painstakingly adjusted (by adding or subtracting varying amounts of the ϕ_j) so as to satisfy a family of orthogonality relations. None of these special considerations is required with the DE-FOP-VIM and the almost-degenerate states can be considered together with the degenerate.

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